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A novel biodegradable nicotinic acid/calcium phosphate composite coating on Mg–3Zn alloy

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ABSTRACT

A novel biodegradable composite coating is prepared to reduce the biodegradation rate of Mg–3Zn alloy. The Mg–3Zn substrate is first immersed into 0.02 mol L^{-1} nicotinic acid (NA) solution, named as vitamin B_3, to obtain a pretreatment film, and then the electrodeposition of calcium phosphate coating with ultrasonic agitation is carried out on the NA pretreatment film to obtain a NA/calcium phosphate composite coating. Surface morphology is observed by scanning electron microscopy (SEM). Chemical composition is determined by X-ray diffraction (XRD) and EDX. Protection property of the coatings is evaluated by electrochemical tests. The biodegradable behavior is investigated by immersion tests. The results indicate that a thin but compact bottom layer can be obtained by NA pretreatment. The electrodeposition calcium phosphate coating consists of many flake particles and ultrasonic agitation can greatly improve the compactness of the coating. The composite coating is biodegradable and can reduce the biodegradation rate of Mg alloys in stimulated body fluid (SBF) for twenty times. The biodegradation process of the composite coating can be attributed to the gradual dissolution of the flake particles into chippings.

1. Introduction

Mg and its alloys are potential biodegradable materials due to their attractive biological properties [1–3]: (1) metal Mg is biodegradable in body fluids by corrosion; (2) Mg^{2+} is harmless to human body; (3) Mg can accelerate the growth of new bone tissue; (4) the density, elastic modulus and yield strength of Mg are closer to the bone tissue than the conventional implants. Thus, Mg and its alloys are attracting great interest as biodegradable implants.

Unfortunately, Mg alloys are susceptible to suffer attack in chloride containing solutions, e.g. the human body fluid or blood plasma [4]. If the Mg alloy implants are used to repair the diseased bone tissue, they are possible to early lose the mechanical properties before healing due to their high corrosion rate. Thus, protective coatings are necessary to slow down the biodegradation rate of Mg alloys. As the medical applications, the protective coatings should possess good bioactivity and biocompatibility as well as biodegradation. Calcium phosphate is the main component of the natural bones and possesses excellent biocompatibility [5]. Thus, the current research mainly focuses on applying calcium phosphate coatings to reduce the biodegradation rate of Mg alloys [6–9]. The methods for preparing calcium phosphate coatings include plasma spraying, sputtering, pulsed laser-deposition, sol–gel, electrophoresis, electrodeposition, chemical conversion treatment and anodizing. [10–12]. Among these methods, plasma spraying, sputtering, and pulsed laser-deposition belong to physical methods, with complex process and high cost. The other methods belong to chemical methods, which are easy preparation and inexpensive. Especially, the electrodeposition technique can be carried out at room temperature (RT). Furthermore, the thickness and chemical composition of the calcium phosphate coatings are controllable by adjusting the electrodeposition conditions. Thus, the electrodeposition of calcium phosphate coatings is widely investigated to reduce the biodegradation rate of Mg alloy implants. Nevertheless, the calcium phosphate coatings are generally porous structure [13], and their protection property to the Mg alloy implants is unsatisfying. The further improvement of the electrodeposition calcium phosphate coatings is necessary. Two approaches are available for this aim. The first one is to use a pretreatment bottom layer to enhance the protection property. The pretreatment bottom layer should be biocompatible. It is known that nicotinic acid (NA) (C_5H_4NCOOH), also known as vitamin B_3, is a good inhibitor and can form different complexes with metals [14]. Besides, NA is very cheap, easily available, and what is the most important, nontoxic. Thus, NA solution is available for preparing a pretreatment bottom layer. The second one is to improve the compactness of the electrodeposition calcium phosphate coatings. Ultrasonic agitation can achieve this aim.

Thus, the present study is an attempt to modify the surface of Mg–3Zn alloys by nicotinic acid pretreatment with subsequent electrodeposition calcium phosphate coating with ultrasonic agitation to reduce the biodegradation rate of Mg–3Zn alloys. This novel process exhibits a promising future in the actual application to the Mg alloy implants of bone screws and plates, etc.

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2. Experimental

The experimental material used for this investigation was Mg–3Zn alloy with nominal composition of 3 wt.% Zn and 97 wt.% Mg. The use of Mg–3Zn alloy is due to the innocuity of Zn to body. All samples with a size of 40×25×2 mm were successively ground to 2000 grit SiC paper, ultrasonically cleaned in 200 mL acetone for 10 min, then dried in cold air. The metallographical microstructure of the Mg–3Zn substrate was etched by the solution consisting of 1 g oxalic acid, 1 mL nitric acid, 1 mL acetic acid and 150 mL distilled water.

Mg–3Zn alloy substrate was immersed into 500 mL NA solution (0.02 mol L^{-1}) at RT for 10 min to obtain a pretreatment film. Then electrodeposition calcium phosphate coating was prepared on the pretreatment film. The electrolyte solution used for the electrodeposition contained 0.1 mol L^{-1} $Ca(NO_3)_2$ and 0.06 mol L^{-1} $NH_4H_2PO_4$ with pH 4.3 adjusted by ammonia liquor. Electrodeposition was carried out using a direct current power at a constant current density of 20 mA cm^{-2} for 30 min at RT. A stainless steel pane was used as anode and the Mg–3Zn alloy sample with NA pretreatment film was used as cathode. Ultrasonic agitation was carried out during the electrodeposition.

The surface morphologies were observed with a Philips XL30 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

The thickness of the composite coating was measured by a 6000-FN1 Eddy current thickness meter. The meter was first calibrated using the Mg–3Zn substrate. Ten spots were measured for every sample and the final result was the average value of ten measurements.

The structure of the calcium phosphate coating was measured using a Philips PW1700 X-ray diffraction (XRD) with Cu target (λ = 0.154 nm). The XRD pattern was analyzed with MDI Jade 5.0 software.

Corrosion resistance was evaluated by electrochemical and immersion measurements. The electrolyte solution used for the corrosion resistance evaluation was simulated body fluid (SBF) [15], which is composed of 8.8 g L^{-1} NaCl, 0.4 g L^{-1} KCl, 0.14 g L^{-1} $CaCl_2$, 0.35 g L^{-1} $NaHCO_3$, 1.0 g L^{-1} $C_6H_6O_6$ (glucose), 0.2 g L^{-1} $MgSO_4 \cdot 7H_2O$, 0.1 g L^{-1} $KH_2PO_4 \cdot H_2O$, 0.06 g L^{-1} $Na_2HPO_4 \cdot 7H_2O$ with pH 7.4 and temperature 37 °C.

Electrochemical measurements were carried out using a classical three-electrode cell with a platinum plate as counter electrode, a saturated calomel electrode as reference electrode and the sample with an exposed area of 1 cm^2 as working electrode. The potentiodynamic curves were obtained using an EG&G potentiostat model 273 (Princeton Applied Research, Oak Ridge, TN, USA). The measurements started from −250 mV vs. open circuit potential (OCP) at a constant scan rate of 0.5 mV s^{-1} and were terminated until a final current density of approximately 10 mA cm^{-2}. The polarization curves were fitted using the CorrView software in the mode of R_p fit. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a model 5210 lock-in amplifier coupled with a potentiostat model 273. An initial delay of 300 s was set to ensure a stable system before undertaking the experiments. The scan frequency ranged from 100 kHz to 10 mHz with a perturbation amplitude of 5 mV.

The Mg–3Zn with and without the NA/calcium phosphate composite coating was immersed in SBF for various durations, and then the surface morphologies were observed by SEM to evaluate the biodegradation behavior. The ratio of sample surface area (cm^2) to the volume of SBF solution (mL) was set to approximately 1:100. Every sample was immersed into 2 L SBF and the SBF was renewed every 8 h to maintain a stable pH level.

3. Results and discussion

3.1. Microstructure of the NA/calcium phosphate composite coating

Fig. 1a shows the microstructure of the Mg–3Zn alloy substrate. It can be found that the surface of the Mg–3Zn alloy is smooth but

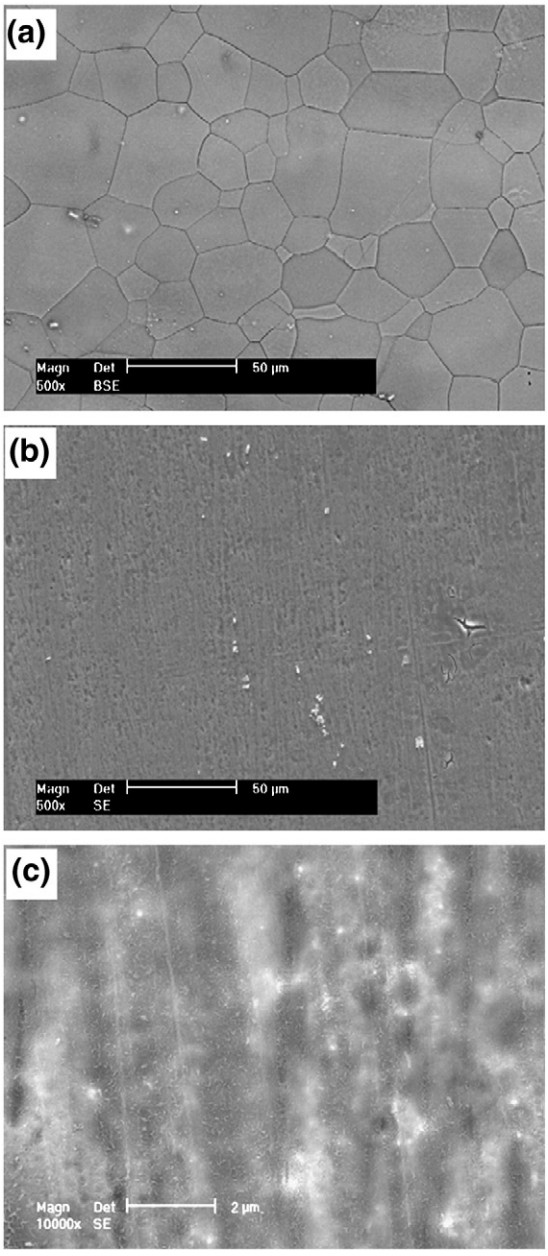

Fig. 1. Surface morphology of (a) Mg–3Zn alloy substrate; (b) and (c) after NA pretreatment.

the grain size is inhomogeneous. The smallest grain size is less than 10 μm and the biggest one is more than 60 μm. The average grain size is approximately 30 μm. After the Mg–3Zn substrate is immersed into 0.02 mol L^{-1} nicotinic acid for 10 min, the microstructure of the Mg–3Zn alloy is changed. Nicotinic acid, a necessary vitamin for body, is a kind of weak acid. It can react with Mg–3Zn substrate to form a protective film. According to the low magnification morphology of the NA pretreatment film (Fig. 1b), some small pits can be observed on the surface. These pits are possible due to the dissolution of Mg–3Zn substrate in NA. The existence of these small pits is beneficial for improving the adhesion of the pretreatment bottom layer with the subsequent electrodeposition calcium phosphate coating. According to the high magnification morphology in Fig. 1c, the pretreatment film is thin and its thickness is difficult to be measured, but this film is compact. On one hand, this thin film can provide protection to the Mg–3Zn substrate. On the other hand, this thin film is conductive, which is available for the subsequent electrodeposition process.